

Thermal fluctuations and nanoscale effects in the nucleation of carbonaceous dust grains

Adam C. Keith, Davide Lazzati

Department of Physics, North Carolina State University, 2401 Stinson Drive, Raleigh, NC 27695-8202

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ABSTRACT

We investigate the role of thermal fluctuations and of the finite number of monomers in small clusters of carbon atoms on the nucleation rate of carbonaceous grains. Thermal fluctuations are due to the quantized nature of the energy exchanges between the clusters, the gas, and the radiation field. Nanoscale effects modify the spontaneous detachment of monomers due to the finite amount of internal energy contained in small clusters. We find that both corrections have a big impact on the stability of the clusters and on the rate of nucleation. We implement our model within a Monte Carlo code to derive the new stability conditions for clusters as well as nucleation rates. Due to computing limitations, we can explore the consequences of this approach only at high temperatures, at which particle interactions are not much less frequent than photon interactions. We found that the combined effect of the detachment correction and the temperature fluctuations produces faster nucleation. We also found that the nucleation rate depends on the composition of the gas and not only on the partial pressure of the compound that condensates into grains. This is a unique result of this model that can be used to prove or disprove it.

Key words: dust, extinction

1 INTRODUCTION

Dust is one of the main constituents of the interstellar medium (ISM), making up to 1 per cent of the baryonic mass of galaxies that is not in stars (Mathis, Rumpl & Nordsieck 1977). The average composition of interstellar dust is made of Polycyclic Aromatic Hydrocarbons (PAHs), carbonaceous grains, and silicates (Weingartner & Draine 2001), each of which contains particles ranging from several angstroms to a few microns in size. Dust plays many important roles in astrophysics: it provides attenuation of radiation (Cardelli, Clayton & Mathis 1989), induces polarization in the optical and UV frequencies (Serkowski, Mathewson & Ford 1975), provides a safe environment for molecular chemistry (Brown 1990), cools protostellar clouds allowing for the formation of population II.5 stars (Schneider et al. 2006), and, finally, provides the building blocks for the formation of terrestrial planets (Lissauer 1993).

Despite such fundamental roles played by dust, the physics of dust nucleation is still highly debated, and the sites, rates, and composition of the dust produced in the different environments are poorly known. Historically, dust nucleation has been treated as an out of equilibrium perturbation of a thermodynamical process (Becker & Doring 1935; Feder et al. 1966; Kashchiev 2000). Under this approach, the dust/vapor mix is assumed to be in thermodynamical equi-

librium and able to exchange energy in a continuous way. A critical cluster size can be identified as the cluster with the highest Gibbs free energy and the nucleation rate is computed as the flow of particles through the critical cluster size (Becker & Doring 1935; Feder et al. 1996; Kashchiev 2000). Even though this “classical” theory can give an explanation to the qualitative features of nucleation (the presence of a threshold below which nucleation is forbidden, the existence of supersaturation, and the steep increase of the nucleation rate with both temperature and saturation), the quantitative comparison between prediction and rates is still problematic (Wölk & Strey 2001). To make things worse, any attempt to improve the theory has resulted in a deterioration of the quantitative comparison.

The adoption of the thermodynamical approach for astrophysical dust nucleation was criticized already by Donn & Nuth (1985) who pointed out problems with the time scale for obtaining thermodynamic equilibrium as well as discrepancies between the theory and experiments. An alternative to the thermodynamical treatment is the kinetic treatment of nucleation (Becker & Doring 1935, Kashchiev 2000). The kinetic theory derives nucleation rates by analyzing the accretion and ejection rates of monomers from sub-critical clusters. The most fundamental difference is that in the kinetic theory the nucleation rate depends on the properties of grains of all sizes (and especially of the unsta-

ble ones) while in the thermodynamic theory the nucleation rate depends only on the properties of the critical cluster. Another advantage of the kinetic theory is that of allowing the consideration of radiation as a player in the nucleation game, as both an energy sink (Lazzati 2008) and as an energy source (this paper). Astrophysical dust nucleation is more complex than lab nucleation (e.g. of water, Wölk & Strey 2001) for at least two reasons. First, the conditions of nucleation in astrophysics are very different from lab conditions and the verification of any theory that predicts nucleation rates of a particular dust compound can be performed only very indirectly. Second, some of the components of interstellar dust, such as silicates, do not have a vapor phase and the nucleation process must include the chemical bonding of the atoms into the basic monomer of the grain. We call this process chemical nucleation to distinguish it from homogeneous nucleation (the nucleation of a vapor on its own liquid or solid phase) and from heterogeneous nucleation (the nucleation of a compound on a different substrate). This difficulty of chemical nucleation has been approached in two ways. Kozasa et al. (1989, 1991, see also Nozawa et al. 2003, 2008, 2010; Todini & Ferrara 2001; Schneider et al. 2004; Bianchi & Schneider 2007) consider the nucleation process as driven by the atom that accretes with the lowest frequency, assuming all other compounds to be already present on the grain surface. It is unclear, however, how the very first molecules are formed and bound together in a sub-critical cluster. Cherchneff et al. (2000) and Cherchneff & Dwek (2009, 2010) consider instead the chemistry of precursor molecules to bridge the gap between atoms in the gas phase and sub-critical clusters onto which the monomers can accrete.

In this paper we address another limitation of the thermodynamical treatment by considering the effect of discreteness in the energy exchange between the clusters, the gas, and the radiation field. We focus on the homogeneous nucleation of carbonaceous grains to avoid the complication of chemical nucleation, and approximate cluster surfaces as spherical to simplify calculations. As a consequence of the quantized nature of cluster-radiation and cluster-atom interactions, the cluster vibrational temperature can grow well above the equilibrium temperature and/or decrease below it. We develop a Monte Carlo code to simulate the thermal history and stability of small clusters and grains and derive nucleation rates. Due to technical computing limitations we can, at present, address only the high temperature regime, since at low temperatures the interactions are overwhelmingly dominated by exchanges of radiation.

This paper is organized as follows: in Section 2 we describe the theory of kinetic nucleation and obtain equations for the temperature fluctuations and ejection rates in small clusters, in Section 3 we describe the results of the Monte Carlo implementation, and in Section 4 we discuss our results.

2 NON-EQUILIBRIUM NUCLEATION

The kinetic approach to nucleation (Becker & Döring 1935; Kashchiev 2000) allows for the computation of nucleation rates in any non-equilibrium condition. The basic requirement is the knowledge of the accretion and ejection rates

of monomers (in our case Carbon atoms) from a cluster or grain.¹

The nucleation rate, i.e., the number of new stable grains formed per unit time and volume, is given by:

$$J = n_X f_1 \left[1 + \sum_{j=2}^{\infty} \left(\prod_{k=2}^j \frac{g_k}{f_k} \right) \right]^{-1} \quad (1)$$

where n_X is the density of monomers in the gas phase and f_i is the rate of the reaction



where X is a monomer and X_i is a cluster that contains i monomers. The rate of the reaction



is instead indicated as g_i .

In an equilibrium situation, where the cluster and the gas are at the same temperature, the attachment rate is given by:

$$f_i = k_s n_X (36\pi)^{1/3} \left(\frac{m_X}{\rho_X} \right)^{2/3} \sqrt{\frac{kT}{2\pi m_X}} i^{2/3} \quad (4)$$

where $k_s \leq 1$ is the sticking coefficient, n_X is the number density of the monomer in the gas/vapor phase, and ρ_X is the density of the solid phase. The detachment rate is instead given by:

$$g_i = k_s n_{X,\text{eq}}(T) (36\pi)^{1/3} \left(\frac{m_X}{\rho_X} \right)^{2/3} \sqrt{\frac{kT}{2\pi m_X}} i^{2/3} \times e^{\left(\frac{32\pi}{3}\right)^{1/3} \left(\frac{m_X}{\rho_X}\right)^{2/3} \frac{\sigma}{kT} i^{-1/3}} \quad (5)$$

where $n_{X,\text{eq}}(T)$ is the density of the gas phase at saturation for the temperature T and σ is the surface tension or surface energy of the condensed phase. The extra exponential term takes into account the increased detachment rate from small cluster due to the effect of surface tension (or surface energy) that decreases the effective binding energy of monomers.

While the attachment f_i only depends on the gas properties (density and temperature), the detachment frequency depends on the cluster properties and can change substantially if the assumption of thermal equilibrium is relaxed. Following Lazzati (2008), we assume that if the grain temperature T_{grain} is different from the gas temperature T_{gas} , the detachment frequency is modified as

$$g_i = k_s n_{X,\text{eq}}(T_{\text{grain}}) (36\pi)^{1/3} \left(\frac{m_X}{\rho_X} \right)^{2/3} \sqrt{\frac{kT_{\text{grain}}}{2\pi m_X}} i^{2/3} \times e^{\left(\frac{32\pi}{3}\right)^{1/3} \left(\frac{m_X}{\rho_X}\right)^{2/3} \frac{\sigma}{kT_{\text{grain}}} i^{-1/3}} \quad (6)$$

i.e., we assume that the detachment rate depends only on the grain properties and not on its surroundings. Later, we will describe an additional modification of the g_i equation to take into account the reduction in detachment rate from very

¹ In this paper we will define a cluster as an unstable group of monomers, with a size smaller than the critical radius. Similarly, we will define a grain as a stable group of monomers, larger than the critical radius. However, when the stability is not the focus of a sentence, cluster and grain are used as synonyms.

small and/or very cold clusters (Guhathakurta & Draine 1989). Once Eq. 6 is established, the challenge is to evaluate the cluster temperature to be used. Lazzati (2008) assumed that the input and output of energy can be considered continuum and found the equilibrium solution, showing that in most cases the cluster stabilizes at a temperature that is smaller than that of the gas, due to the increased radiation losses. In this paper, we improve on that assumption by considering the quantized nature of the energy exchanges between the cluster, the gas, and the radiation field. We consider five interactions responsible for altering the thermal state of the cluster:

- attachment of a monomer to the cluster
- detachment of a monomer from the cluster
- collision between the cluster and an atom/molecule of an inert carrier gas
- absorption of a photon
- emission of a photon

Due to the statistical nature of the occurrence of all the above processes, we include them in a Monte Carlo code. At each iteration, the code stochastically selects the event that would occur first. For that iteration, energy conservation laws are applied to determine the thermal state of the cluster after the selected event occurs. The temperature change is computed through the change of internal energy, ΔU . The cluster size is also modified if an attachment or detachment event occurs.

2.1 Monomer Attachment

The rate of attachment of monomers is given by Eq. 4. The change of internal energy for a monomer attachment has two components: the kinetic energy gained from the incoming monomer and the binding energy that is released at the attachment:

$$\Delta U_{\text{Att}} = KE(T_{\text{gas}}) + E_{\text{Bind}}(i \rightarrow i + 1) \quad (7)$$

where the kinetic energy $KE(T_{\text{gas}})$ is randomly drawn from a Maxwell-Boltzmann distribution at the gas temperature T_{gas} , and $E_{\text{Bind}}(i) = iE_{\text{Bind,blk}} - \sigma S(i)$ is the total binding energy released in the assembly of i monomers into a cluster with surface $S(i)$ and binding energy $E_{\text{Bind,blk}}$ for a monomer in the bulk. Thus, the binding energy for an attachment is computed as:

$$\begin{aligned} E_{\text{Bind}}(i \rightarrow i + 1) &= \\ [(i + 1)E_{\text{Bind,blk}} - \sigma S(i + 1)] - [iE_{\text{Bind,blk}} - \sigma S(i)] &= \\ E_{\text{Bind,blk}} - \sigma [S(i + 1) - S(i)] &= \\ E_{\text{Bind,blk}} - \sigma (36\pi)^{1/3} \left(\frac{m_X}{\rho_X} \right)^{2/3} [(i + 1)^{2/3} - i^{2/3}] \end{aligned} \quad (8)$$

where we have used the relation $S(i) = (36\pi)^{1/3} \left(\frac{m_X i}{\rho_X} \right)^{2/3}$.

2.2 Monomer Detachment

Similarly, the change of internal energy for a monomer detachment has two components: the kinetic energy lost from the outgoing monomer and the binding energy required to separate the monomer from the cluster:

Symbol	Meaning
b	Minimum number of quanta to eject a monomer
C_{abs}	Correction term for Photon Absorption
C_{emis}	Correction term for Photon Emission
C_q	Correction term for Monomer Detachment
d_f	Number of degrees of freedom
E_{Bind}	Binding energy
$E_{\text{Bind,blk}}$	Binding energy of a bulk monomer
f_i	Attachment rate of monomers onto a cluster of size i
g_i	Detachment rate of monomers from a cluster of size i
h_i	Collision rate of inert gas atoms with a cluster of size i
H/C	Hydrogen/Carbon number density ratio
i_C	Critical cluster size
J	Nucleation rate
KE	Kinetic energy of a monomer or inert gas particle
k_s	Sticking coefficient
m_{CG}	Mass of an inert gas particle
m_X	Mass of the monomer
n_{CG}	Number density of carrier gas
n_X	Number density of monomers in the gas phase
$n_{X,\text{eq}}$	Number density of monomers in the gas phase at vapor pressure
$P(\nu, i)$	Modified Blackbody Distribution
q	Total number of quanta in a cluster
S	Gas saturation
$S(i)$	Surface area of cluster containing i monomers
T_{gas}	Temperature of the gas
T_{grain}	Temperature of the grain
T_{rad}	Temperature of the radiation field
U	Internal energy
X	Monomer
X_i	Cluster containing i monomers
α_i	Photon Absorption rate of a cluster of size i
ΔU_{Att}	Change of internal energy for monomer attachment
$\varepsilon(\nu, i)$	Emissivity, frequency and size dependent
γ_i	Photon Emission rate of a cluster of size i
ρ_X	Density of the condensed phase
σ	Surface energy (tension) of the condensed phase
σ_{SB}	Stefan-Boltzmann constant
ω_0	Frequency of harmonic oscillators in the Einstein model

Table 1. Glossary of used symbols

$$\Delta U_{\text{Det}} = -KE(T_{\text{grain}}) + E_{\text{Bind}}(i \rightarrow i - 1) \quad (9)$$

where the kinetic energy $KE(T_{\text{grain}})$ is randomly drawn from a Maxwell-Boltzmann distribution at the grain temperature T_{grain} . So, the binding energy is:

$$\begin{aligned} E_{\text{Bind}}(i \rightarrow i - 1) &= \\ [(i - 1)E_{\text{Bind,blk}} - \sigma S(i - 1)] - [iE_{\text{Bind,blk}} - \sigma S(i)] &= \\ -E_{\text{Bind,blk}} - \sigma [S(i - 1) - S(i)] &= \\ -E_{\text{Bind,blk}} - \sigma (36\pi)^{1/3} \left(\frac{m_X}{\rho_X} \right)^{2/3} [(i - 1)^{2/3} - i^{2/3}] \end{aligned} \quad (10)$$

again for $S(i) = (36\pi)^{1/3} \left(\frac{m_X i}{\rho_X} \right)^{2/3}$.

The rate of detachment of monomers from big grains is given by Eq. 5. However, as previously mentioned, g_i requires a modification to correctly describe detachment from very small and/or very cold clusters. As Guhathakurta & Draine (1989) realized, clusters must have at least enough internal energy to supply a single particle within the grain with at least the binding energy to eject that particle from the cluster. However, even if the internal energy of the cluster is above this threshold, we cannot be certain that this

energy will break the bond of a single monomer. In order to determine the probability that this could happen, we must introduce quantization of energy, modelling clusters as Einstein solids, such that X_i has $d_f = 3i - 6$ vibrational degrees of freedom. Assuming that these degrees of freedom are harmonic oscillators with common frequency $\omega_0 = 0.75kT_{Debye}$ and average energy $\hbar\omega_0$, and given the internal energy U of the cluster, we can determine the total number of quanta in the cluster, $q = U/\hbar\omega_0$, as well as the number of quanta required to eject a monomer, $b = E_{\text{Bind}}/\hbar\omega_0$. Using a combinatorial approach with the preceding values, we calculate the probability that one degree of freedom has *at least* b quanta. This (see Guhathakurta & Draine 1989) reduces the monomer detachment rate by:

$$C_q = \left(\frac{d_f}{q} + 1\right)^b \frac{q!(q - b + d_f - 1)!}{(q + d_f - 1)!(q - b)!} \quad (11)$$

where $\left(\frac{d_f}{q} + 1\right)^b$ is the normalization factor for $d_f \rightarrow \infty$. Thus, the new detachment rate is simply:

$$g_i^* = C_q g_i \quad (12)$$

If we define $y \equiv q/d_f$ as the average number of quanta per degree of freedom, C_q is nearly unity when $y \gg b$ while $C_q \rightarrow 0$ as $y \rightarrow 0$ or $q \rightarrow b$; consequently, for $q < b$, $g_i^* = 0$ and monomers cannot be ejected from the cluster.

2.3 Inert Carrier Gas Collision

Even though we focus on homogeneous nucleation, we also consider collisions with inert particles, such as hydrogen atoms, that are inevitably mixed in the surrounding gas in any astrophysical setting. We model this interaction as an event in which the particle exchanges energy with the cluster and rebounds with a new velocity distribution. The rate of inert collisions is as follows:

$$h_i = k_s n_{\text{CG}} (36\pi)^{1/3} \left(\frac{m_X}{\rho_X}\right)^{2/3} \sqrt{\frac{kT_{\text{gas}}}{2\pi m_{\text{CG}}}} i^{2/3} \quad (13)$$

Although similar to f_i , this rate is dependent on the number density of the inert gas, n_{CG} and on the mass of a single gas particle. The change of internal energy for an inert collision is simply the change in kinetic energy after the collision:

$$\Delta U_{\text{Col}} = KE(T_{\text{gas}}) - KE(T_{\text{grain}}) \quad (14)$$

where both $KE(T_{\text{gas}})$ and $KE(T_{\text{grain}})$ are randomly drawn from Maxwell-Boltzmann distributions at the gas temperature T_{gas} and grain temperature T_{grain} , respectively. We make the approximation that as the inert gas particle comes in contact with the cluster, it immediately attains the cluster's temperature, and rebounds with that dependency. Even though this is only an approximation, it ensures that over many collisions thermal equilibrium is established.

2.4 Photon Absorption

The rate at which the cluster absorbs photons is derived from an integrated form of the Planck law, given by:

$$\alpha_i = 0.37(36\pi)^{1/3} C_{\text{abs}} \left(\frac{m_X}{\rho_X}\right)^{2/3} \frac{\sigma_{\text{SB}} T_{\text{rad}}^3}{k} i^{2/3} \quad (15)$$

where C_{abs} is the correction term resulting from the fact that clusters do not behave as blackbodies. This term is calculated by:

$$C_{\text{abs}} = \int \frac{\varepsilon(\nu, i) \nu^2 d\nu}{e^{\frac{h\nu}{kT_{\text{rad}}}} - 1} \bigg/ \int \frac{\nu^2 d\nu}{e^{\frac{h\nu}{kT_{\text{rad}}}} - 1} \quad (16)$$

where $\varepsilon(\nu, i) \leq 1$ is the emissivity of the material, dependent on the size of the cluster, and the frequency of radiation (Draine & Lee 1984; Laor & Draine 1993). For small grains, C_{abs} severely reduces the rate of photon absorption as the cluster only significantly interacts with a few frequencies.

The change in internal energy for a photon absorption is given by:

$$\Delta U_{\text{Abs}} = h\nu(T_{\text{rad}}) \quad (17)$$

where ν is randomly drawn from the modified blackbody distribution at the radiation field temperature T_{rad} , given by:

$$P(\nu, i) \propto \frac{\varepsilon(\nu, i) \nu^2}{e^{\frac{h\nu}{kT_{\text{rad}}}} - 1} \quad (18)$$

2.5 Photon Emission

The rate at which the cluster emits photons is analogous to the rate of photon absorption:

$$\gamma_i = 0.37(36\pi)^{1/3} C_{\text{emis}} \left(\frac{m_X}{\rho_X}\right)^{2/3} \frac{\sigma_{\text{SB}} T_{\text{grain}}^3}{k} i^{2/3} \quad (19)$$

except that it is evaluated at T_{grain} and C_{emis} is given by:

$$C_{\text{emis}} = \int \frac{\varepsilon(\nu, i) \nu^2 d\nu}{e^{\frac{h\nu}{kT_{\text{grain}}}} - 1} \bigg/ \int \frac{\nu^2 d\nu}{e^{\frac{h\nu}{kT_{\text{grain}}}} - 1} \quad (20)$$

The change in internal energy for a photon emission is:

$$\Delta U_{\text{Emit}} = -h\nu(T_{\text{grain}}) \quad (21)$$

where ν is instead randomly drawn from the modified blackbody distribution at the grain temperature T_{grain} :

$$P(\nu, i) \propto \frac{\varepsilon(\nu, i) \nu^2}{e^{\frac{h\nu}{kT_{\text{grain}}}} - 1} \quad (22)$$

2.6 Grain Temperature

After each event, the internal energy of the cluster/grain is updated according to the above equations. Once the internal energy is known, the temperature of the cluster/grain can be calculated if the specific heat of the material is known. The new temperature is then fed back into the rate equations, a new event is computed and the cycle is repeated until either the cluster evaporates or grows into a stable grain.

3 MONTE CARLO CALCULATIONS

The physical process described above can be implemented in a Monte Carlo computer code to follow the random oscillations of the grain temperature and the grain fate under the various driving forces. Here and in the following, we apply the theory described above to clusters of carbon atoms,

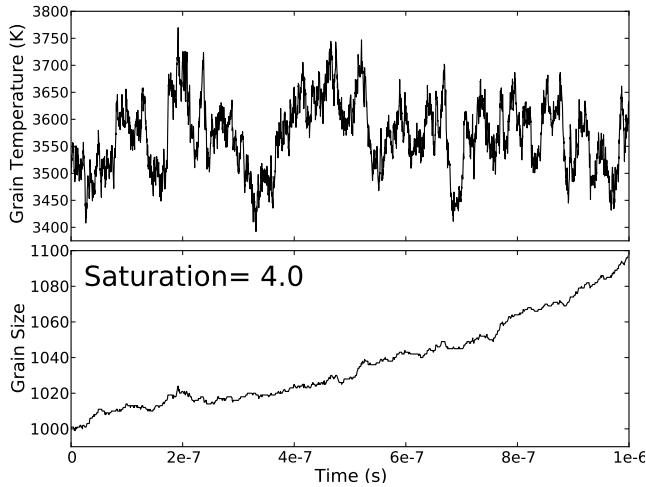


Figure 1. Temperature and size evolution of a grain initially composed of 1000 carbon atom immersed in a hydrogen-carbon gas with $H/C = 100$, $T_{\text{gas}} = 3500$ K, and with saturation $S = 4$.

precursors of carbonaceous dust grains. We adopt the absorption coefficients for graphite grains from Draine & Lee (1984) and Laor & Draine (1993), extrapolating their result to smaller grains when necessary. The other graphite properties we adopt and relevant references are summarized in Table 2.

An example of the thermal history of a relatively big carbonaceous grain is shown in Figure 1, where a grain of initially 1000 carbon atoms is left free to evolve in a hydrogen-carbon gas with number density ratio $H/C = 100$, temperature $T_{\text{gas}} = 3500$ K, and saturation $S = 4$. The grain is observed to grow as its temperature fluctuates with excursions as large as 200 K, or ~ 5 per cent of the grain temperature. Figure 2 shows instead the much more violent thermal history of a small grain, injected in the same gas. In this case the temperature can fluctuate by more than 100 per cent. Even under such violent fluctuations, the grain eventually grows to a larger size.

3.1 Grain Stability

An important consequence of our analysis of the fluctuations of the grain temperature under the effect of quantized energy exchanges with the gas and the radiation field is that the grain stability becomes a statistical concept instead of an exact concept. In the classical approach, when the Gibbs free energy is maximized, the grain is supposed to be in an unstable but exact equilibrium, able to remain at the stable size forever. Any cluster smaller than the critical size is doomed to evaporate and any grain bigger than the critical size will eventually grow. In our approach, two grains of the same size can be in different stability conditions (one stable and the other unstable) if they are at different temperatures. Moreover, a grain that is stable can become an unstable cluster without changing its size by absorbing a photon that raises its temperature and vice versa. A critical size that depends only on the gas temperature and saturation - reminiscent of the one of the classical theory - can be defined as the size for which the probability of eventual

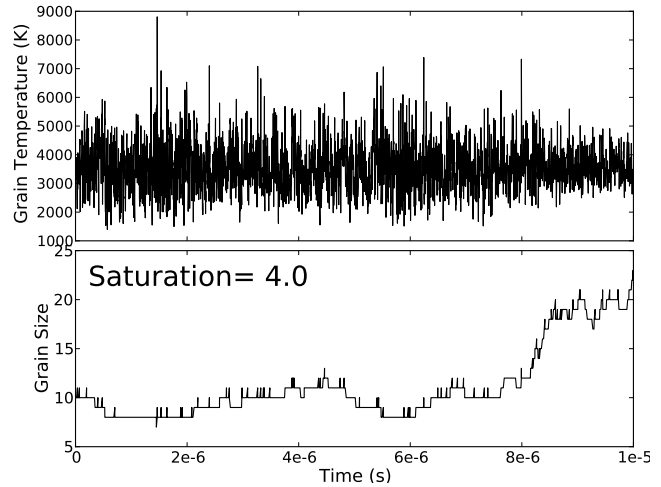


Figure 2. Same as Fig. 1 but for an initially smaller grain made by 10 carbon atoms.

evaporation is the same as the probability of eventual growth into a stable grain.

Here we discuss stability by finding the saturation at which a certain cluster becomes stable, according to the above definition. Unfortunately the photon absorption interactions become so numerous at low temperatures ($T_{\text{gas}} < 2500$ K) that running the code until a statistically sound number of C atom attachments or detachments is observed becomes practically unfeasible. For that reason, in the following we concentrate on the high temperature nucleation.

Classically, the saturation at which a cluster with size i is stable, or critical, is given by:

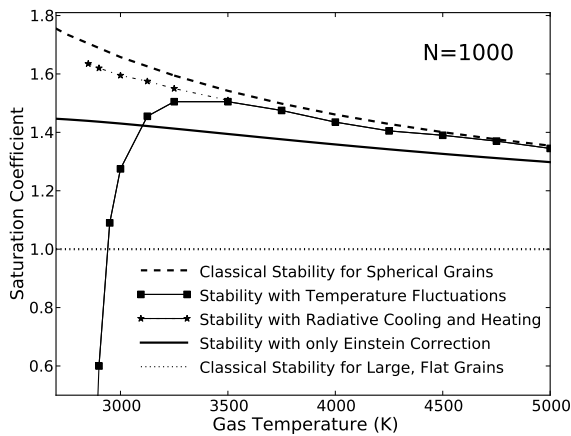
$$S = e^{\left(\frac{32\pi}{3}\right)^{1/3} \left(\frac{m_X}{\rho_X}\right)^{2/3} \frac{\sigma}{kT_{\text{grain}}}} i^{-1/3} \quad (23)$$

Since T_{grain} is not constant in our approach, we determine the stability saturation for a given cluster at a specific gas temperature by proceeding iteratively as follows. We start from a fairly large saturation (e.g. $S = 10$) and perform a minimum of 10 simulations in which the grain may evolve at that saturation. Each simulation is halted when the initial cluster has changed its size by at least 10 per cent². If all or most of the simulations resulted in grain growth, the estimated saturation was too large, and if all or most of the simulations resulted in grain evaporation, the estimated saturation was too small. We adjust our estimate of the critical cluster size and repeat the process, narrowing in on the saturation for which half of the clusters grow and half evaporate. In this way we can obtain a new stability curve, i.e., the location in the $T_{\text{gas}} - S$ plane where a grain of a given size has the same probability of growing or evaporating. This is analogous to the critical cluster size in the classical nucleation theory. Thus, if the gas saturation is greater than the stable saturation the grain is more likely to grow.

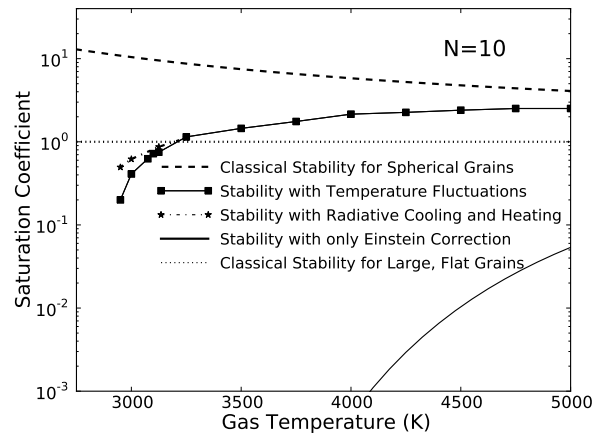
The stability plot for clusters with $i = 1000$ is shown in Figure 3. For all gas temperatures, the new stability

² For large clusters ($i \geq 100$) this is more than enough to determine the final fate of the cluster. However, for small grains we halt the simulations after a 70 per cent change of the cluster initial size.

Property	Notes
$\sigma = 1500 \text{ erg cm}^{-2}$	Surface energy (Tabak et al. 1975)
$\rho = 2.23 \text{ g cm}^{-3}$	Density of graphite
$m_C = 1.9944 \cdot 10^{-23} \text{ g}$	Mass of one carbon atom
Eq. 3.3 of Guhathakurta & Draine (1989)	Heat capacity
$T_{\text{Debye}} = 420 \text{ K}$	Debye temperature (Guhathakurta & Draine 1989)
$n_{X,\text{eq}} = \frac{6.9 \cdot 10^{13} e^{-\frac{844282}{T_{\text{grain}}}}}{k T_{\text{grain}}} \text{ cm}^{-3}$	Equilibrium gas density
$E_{\text{Bind,blk}} = 1.1831760 \cdot 10^{-11} \text{ erg}$	Bulk binding energy of graphite

Table 2. Graphite properties used in this paper.**Figure 3.** Stability plot in the $T_{\text{grain}} - S$ plane for a carbonaceous cluster with $i = 1000$ carbon atoms immersed in a hydrogen-carbon gas with $H/C = 100$. Both the solid line with square markers and the dash-dot line with star markers, show the results of this paper. Actual calculations were performed only at the marked locations. Both lines show stability with temperature fluctuations, however, the solid line does not include an external radiation field, while the dash-dot line does, incorporating the heating effect of photons. The radiation field is assumed to be a black body at the temperature of the gas. For higher temperatures, radiation effects become negligible and the lines converge. The dashed line shows the stability for spherical clusters in the classical approximation in which the temperature of the cluster is constant and equal to the temperature of the gas. The thick solid line shows instead the stability line if the Einstein model is applied to the standard theory but temperature fluctuations are neglected.

curve is lower than in the standard theory, generally allowing lower saturations in which clusters can grow. This is a result of three competing effects. At high temperatures ($T_{\text{gas}} > 3000 \text{ K}$) the strongest effect is the Einstein model correction that makes the clusters much more resilient to evaporation. At lower temperatures, the grains are made more stable (even more than the Einstein correction prediction) by the fact that their temperature is lower than the gas temperature (Lazzati 2008). Both these stabilizing effects are balanced by the effect of temperature fluctuations that tend to make clusters unstable. The drop of the stability line at low temperatures is expected to be reduced in the situation in which the radiation field is dense, so that interactions mediated by photons can also have a heating effect, as well as a cooling effect. In the case of a blackbody radiation field in thermal equilibrium with the gas, the drop

**Figure 4.** Same as Figure 3 but for a smaller cluster with $i = 10$ carbon atoms. Even with the effect of an external radiation field (stars) the Einstein correction dominates.

is absent, as shown by the star symbols in Figure 3. This last condition may be relevant for dust production in a supernova explosions.

Figure 4 shows instead the stability line for smaller clusters with $i = 10$ carbon atoms. In this case, the Einstein correction term has a big influence, allowing its effect to dominate over the entire temperature range that we investigated. Even the heating effect of a radiation field in thermal equilibrium with the gas does little to diminish the effect of the Einstein model correction (see the star symbols in Figure 4). This steep drop makes determining stability for lower temperature more difficult. Also, smaller clusters are more susceptible to random fluctuations, inherent in our code, requiring more simulations, at least a minimum of 30, to determine the new stability curve.

Another way to look at cluster stability and critical cluster size is to plot the attachment and detachment rates as a function of cluster size for given conditions of gas temperature and saturation. With the use of a Monte Carlo code like ours it is not straightforward to compute the average detachment rate for a given cluster size. That is because in a run, the cluster size varies (see Figure 1 and 2). In order to compute the average detachment rate from a cluster of a given size i we run the code artificially maintaining the cluster size constant. When an attachment happens, we compute the temperature that the $i + 1$ cluster would attain, but we keep the size equal to i . Analogously, when a detachment happens, we compute the temperature that the $i - 1$ cluster

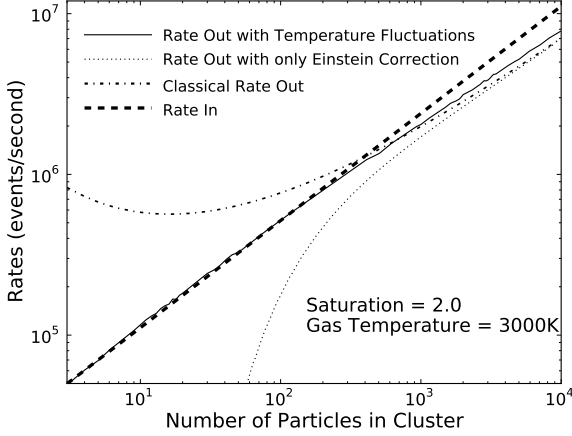


Figure 5. Attachment and detachment rates from carbonaceous clusters for $S = 2$ saturation and gas temperature $T_{\text{gas}} = 3000$ K.

ter would have but we maintain the size constant to i . This artificial forcing is equivalent to assuming that the temperature distribution of the size i cluster is not different from the temperature distribution of the $i - 1$ and $i + 1$ clusters.

Figure 5 shows attachment and detachment rates from clusters containing between $i = 3$ and $i = 10000$ carbon atoms embedded in a saturation $S = 2$ hydrogen-carbon gas with $H/C = 100$ and temperature $T_{\text{gas}} = 3000$ K. The attachment rate is shown as a thick dashed line while detachment rates for different assumptions are overlaid. The classical detachment rate is shown with a dash-dot line, yielding a critical cluster of $i_C = 350$ carbon atoms. The dotted line shows the predicted rate if the Einstein model is considered but thermal fluctuations are neglected. The graph clearly shows that by itself the Einstein correction is too strong, making even the smallest clusters stable at a modest saturation. This would result in a catastrophic nucleation of very small grains. The detachment rate with thermal fluctuations included is shown with a black line. Interestingly, the attachment and detachment rates almost trace each other for the small, unstable clusters. This results from the fact that the biggest thermal fluctuations are due to the attachment-detachment process, since the binding energy is typically much larger than the photon and collision energies. As a consequence, an attachment results in a sharp increase in the cluster temperature that increases the detachment rate by a large factor, increasing the probability of a detachment, which in turn cools the cluster significantly. This locking of the attachment and detachment events is particularly evident for pure gases and for $k_s = 1$, in which every collision of the cluster is with a monomer that attaches to the cluster. Less pure gases show this tracking to a lesser extent (typically only for small clusters). In terms of the critical cluster size, we see that the critical cluster is smaller than the one predicted classically, but not by a huge factor. The complete theory with fluctuations predicts a critical cluster of approximately $i_C = 100$ carbon atoms.

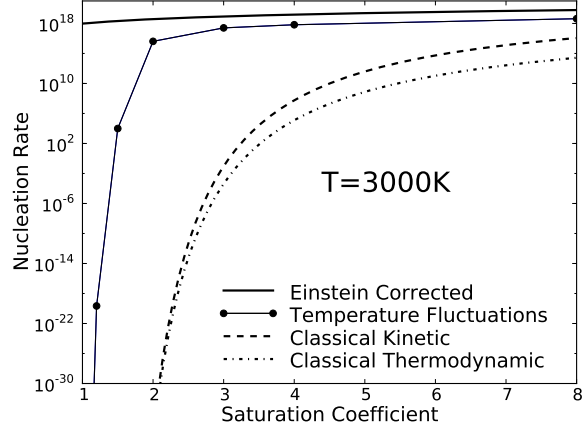


Figure 6. Nucleation rate as a function of saturation for carbonaceous grains from a hydrogen-carbon gas with $H/C = 100$ and temperature $T_{\text{gas}} = 3000$ K.

3.2 Nucleation Rates

Once the average rates out for all sizes between $i = 3$ and approximately twice the critical size have been computed, the nucleation rate can be calculated with a modification of Eq. 1:

$$J = \frac{n_X}{2} f_2 \left[1 + \sum_{j=3}^{2i_C} \left(\prod_{k=3}^j \frac{g_i}{f_i} \right) \right]^{-1} \quad (24)$$

Since the detachment rate is always significantly less than the attachment rate for $i = 2$, due either to linearity of the molecular bond (thus a dramatic change in the internal energy) or from a drastic drop associated with the Einstein correction term, we realize that we cannot clearly define a nucleation rate directly from the gas phase. Instead, we assume that all of the gas particles have formed $i = 2$ clusters, and compute J using half of the number density of the gas. The extreme robustness of the $i = 2$ clusters is probably due to the failure of the capillary approximation for very small clusters, as discussed below.

Figure 6 shows the rates computed with our Monte Carlo code compared with rates obtained by other methods. The dash-dot line shows the rate obtained from the thermodynamic approach (e.g. Kozasa et al. 1989, 1991; Todini & Ferrara 2001; Nozawa et al. 2003, 2008, 2010), while the dashed line shows the rate obtained from the kinetic theory under the assumption of thermal equilibrium between the cluster and the gas. A solid line shows the nucleation rate if the Einstein model correction is taken into account, but thermal fluctuations are neglected. As expected, this rate is very high since the correction makes clusters of all sizes stable. Finally, a solid line with circles shows the result with temperature fluctuations. Since, as we saw before, the combined effect is that of making the clusters more stable, the nucleation rate is significantly larger than the classical result, especially at moderate saturation. Figure 7 shows the same results for a hotter gas with $T_{\text{gas}} = 4000$ K. Finally, Figure 8 shows a contour plot of the nucleation rate as a function of both gas temperature and saturation. It appears that the nucleation rate is highly dependent on temperature

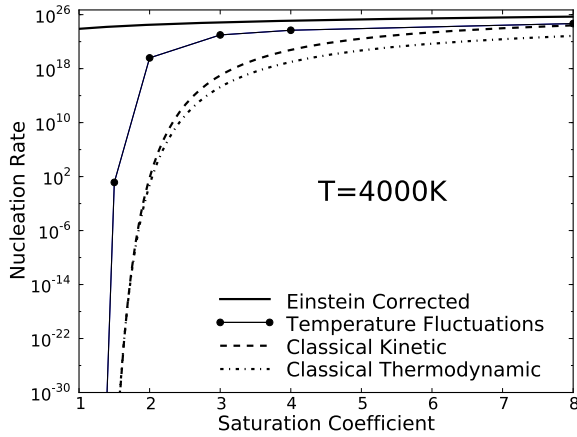


Figure 7. Same as Figure 6 but for a gas at temperature $T_{\text{gas}} = 4000$ K.

at high saturations, but becomes increasingly dependent on saturation as the threshold $S = 2$ approaches.

A final, important result, if not the most important result of this work, is shown in Figures 9 and 10. The figures show the nucleation rate of carbonaceous grains as a function of the carbon concentration in the gas, for $10 < H/C < 300$ and for various saturation values. According to the classical theory, both thermodynamic and kinetic, the nucleation rate should only depend on the partial pressure (or partial density) of the compound that participates in the nucleation, carbon in our case. Instead, we see that if thermal fluctuations are relevant, the nucleation rate depends quite strongly on the concentration. The dependence of nucleation rate on concentration is complex and not straightforward to interpret. For low saturation, the nucleation rate decreases as the relative density of the carrier gas increases, i.e., a pure carbon gas nucleates much faster than a mixed gas (Figure 9). At intermediate saturations, the fastest nucleation is observed at intermediate concentrations ($H/C \sim 50$ for $S = 4$, lower panel of Figure 10). Finally at high saturations, the nucleation rate increases at low concentrations (or high H/C values). The trend seen in Figure 9 at low saturations is easy to explain. The presence of carrier gas particles creates a thermal contact between the cluster and the gas that established thermal equilibrium without requiring growth or evaporation, breaking the strict growth \rightarrow heating \rightarrow evaporation \rightarrow cooling \rightarrow growth behavior outlined above and making the clusters more vulnerable. The trends observed in Figure 10 are instead more difficult to fully understand. Inspection of the rate plots (analogous to Figure 5) suggests that the increase of the nucleation rate is due to the behavior of the grains just above the critical size rather than to the attachment and detachment rates from sub-critical clusters.

4 DISCUSSION

We have presented a model for the physics of the nucleation rate of dust grains from the gaseous phase that includes the role of thermal fluctuations of the clusters as well as

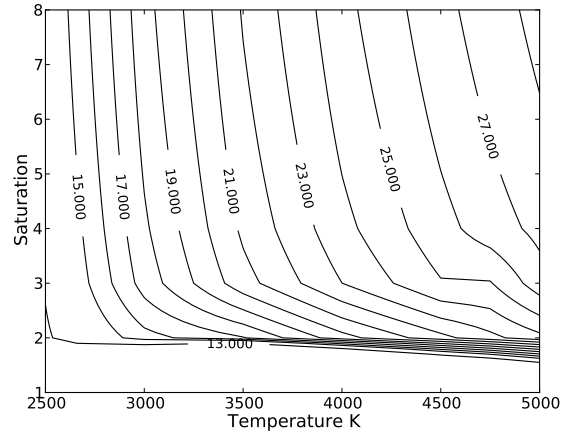


Figure 8. The log of the nucleation rate for carbonaceous grains from a hydrogen-carbon gas with $H/C = 100$.

corrections for the detachment rates from nanoscale clusters. Our implementation is based on the kinetic theory of nucleation (Becker & Döring 1935, Kashchiev 2000), but incorporates some fundamental changes in the way in which the thermal balance of the forming clusters is considered. First, we included a modification to the detachment rates from small grains, following the Einstein model developed by Guhathakurta & Draine (1989). This is a stabilization effect that takes into account the fact that very small grains at low temperature need to use a large fraction of their total internal energy to brake a bond and eject a monomer. As a consequence, the ejection rate does not scale linearly with the surface but becomes very small for small grains. In addition, we consider the fluctuations of the grain temperature as the grain exchanges energy with the gas and the radiation field. Since all the energy exchanges are quantized (through photons or collisions), the temperature of the clusters does not attain an equilibrium value but rather continuously fluctuates around it. We find that the combination of these two effects results in an increased tendency of the clusters to grow, and as a consequence, yields higher nucleation rates. We also find that the nucleation rate depends on the concentration of the nucleating compound in the inert carrier gas, with higher rates for higher concentrations, especially at moderate saturation. This is a new result that has not been predicted by any other theory and can potentially become a crucial test for this model.

Our study has, like most nucleation studies, some important limitations that deserve some discussion and could sizably affect the numerical values of the critical clusters and nucleation rates.

- First, we were able to numerically implement the theory only for high temperatures, for which the rate of particle interactions (cluster-monomer or cluster-carrier gas) outnumber the radiation interactions (carrier-photon). We cannot therefore give any result for the interesting cold temperature regime, where supercooling of the cluster can happen, as discussed in Lazzati (2008). A possible solution for the low temperature regime is to treat radiation interactions as continuous and concentrate on the quantized nature of

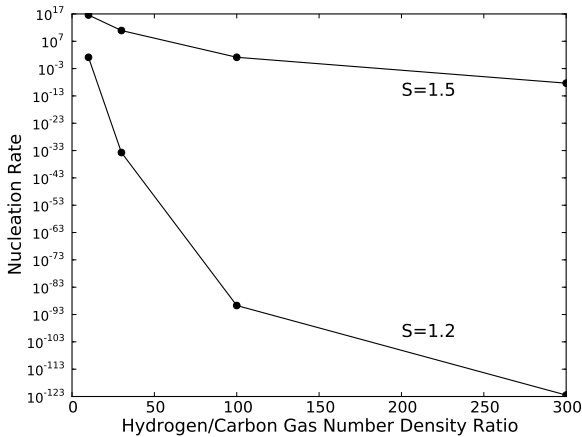


Figure 9. Nucleation rate as a function of the carbon concentration in the gas phase for a hydrogen-carbon gas at saturations 1.2 and 1.5 and temperature 4000 K. For low saturations, higher H/C ratios drastically lower nucleation rates.

the particle interactions only. Such implementation is under study.

- More fundamentally, we have been implicitly adopting the capillary approximation, i.e., we have assumed that the surface energy of graphite clusters is the same of the one of big graphite chunks and we have assumed that the concept itself of surface energy applies to clusters as small as a handful of carbon atoms, for which a surface is a hard concept to define. It is likely that this results in an overestimate of the binding energies of small clusters, ultimately resulting in an overestimate of the nucleation rate.

- Another potential overestimating factor is that we assumed the sticking coefficient to be $k_s = 1$, i.e., all incoming monomers that collide with the cluster stick to it and make the cluster grow. The nucleation rate is directly proportional to the sticking coefficient and, since $k_s \leq 1$, our nucleation rates are overestimated if the real coefficient is different from 1. In addition, reality is likely more complex. k_s is probably dependent on the number of atoms in the cluster. Clusters that fill all the bonds of carbon atoms (such as fullerenes, for example), are likely to have very small values of k_s since it is hard to make them grow beyond their closed structure. An i -dependent value of k_s would, again, result in a decrease of the nucleation rate.

- We have neglected the possibility of cluster-cluster interactions. Even though these should not be numerous, they can be relevant for a particularly pure gas of the nucleating compound.

- We have assumed that even the smallest clusters emit continuum radiation. It is instead likely that they will emit radiation in bands becoming more and more narrow as the size decreases.

- We have assumed that all the energy released as a bonding of a new monomer happens is transformed into internal energy of the cluster/grain. However, it is possible that some of that energy is carried away by a photon. If this were true, smaller temperature fluctuations would be seen in consequence of attachments of new monomers.

Despite all these limitations, we believe the two main

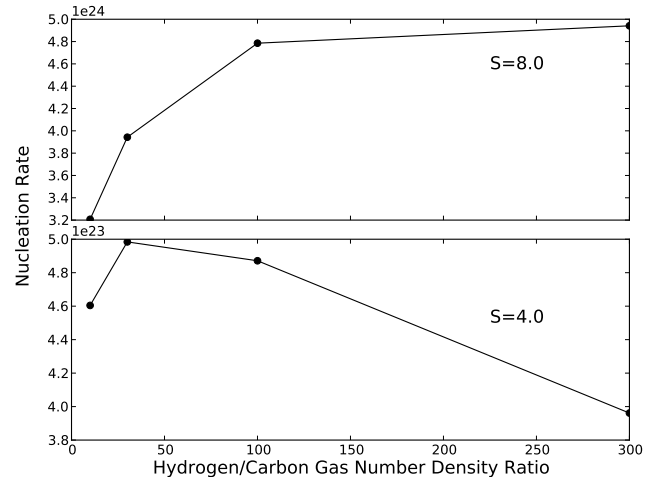


Figure 10. Nucleation rate as a function of the carbon concentration in the gas phase for a hydrogen-carbon gas at saturations 4.0 and 8.0 for 4000 K. There appears to be a transition such that higher saturations instead allow higher H/C ratios to increase nucleation rates.

conclusions of this work hold. First, thermal fluctuations are important in the nucleation process. Second, if this is true, the nucleation rate should depend on the concentration of the nucleating compound. The difference of the nucleation rates resulting from different theories should warn us that a lot has still to be learned in this fascinating field and conclusions based on the blind application of classical nucleation rates should be taken with care.

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